06-05-00

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33591US1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: John D. Hottovy, Harvey D. Hensley, David J. Przelomski, Teddy H. Cymbaluk, Robert K. Franklin, III, and Ethelwoldo P. Perez

Prior Application: 08/893,200
Examiner: C. Lu Rutt
Group Art Unit: 1713

For: HIGH SOLIDS SLURRY POLYMERIZATION APPARATUS

JC542 U.S. PTO 09/586370 06/02/00

REQUEST UNDER 37.C.F.R. 1.53(b) FOR FILING DIVISIONAL APPLICATION

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

This is a request for filing a divisional application under 37 C.F.R. 1.53(b), of pending prior application Serial No. 08/893,200 filed on July 15, 1997, for HIGH SOLIDS SLURRY POLYMERIZATION.

1. Enclosed are true copies of the prior application and the declaration as originally filed. This application contains 5 sheets of drawings.

2. The filing fee is calculated below:

CLAIMS AS FILED IN THE PRIOR APPLICATION, LESS ANY CLAIMS CANCELLED BY THE PRELIMINARY AMENDMENT				
For	Number Filed	Number Extra	Rate	Basic Fee $760.00
Total Claims	13-20	0	X $18.00	$000.00
Independent Claims	3-3	0	X $78.00	000.00
Multiple Dependent Claims	0	0	X $260.00	$000.00
			TOTAL FILING FEE	$760.00

3. Please charge Deposit Account 16-1575 in the amount of the total filing fee stated above. The Commissioner is hereby authorized to charge any additional fees which may be required under 37 C.F.R. 1.16 or 37 C.F.R. 1.17, or credit any overpayment, to Deposit Account 16-1575, but is not authorized to charge any fee provided for under 37 C.F.R. 1.18.

4. The prior application is assigned of record to Phillips Petroleum Company, Bartlesville, Oklahoma, by an Assignment filed in the United States Patent and Trademark Office on July 15, 1997, and recorded on reel 8703, frame 0039.

5. The power of attorney in the prior application is to Richmond, Hitchcock, Fish & Dollar, Registration No. 20,286, P.O. Box 2443, Bartlesville, Oklahoma 74005.

a. The power appears in the original papers in the prior application.

b. All future communications are to be addressed to Richmond, Hitchcock, Fish & Dollar, P.O. Box 2443, Bartlesville, Oklahoma 74005.

6. The art of record in the prior application Serial No. 08/893,200 is drawn to the Examiner's attention. The art does not in the opinion of the undersigned anticipate this invention or render this invention obvious to one of ordinary skill in the art.

7. I hereby certify that the attached papers are true copies of the prior application Serial No. 08/893,200 as originally filed July 15, 1997.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

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CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Assistant Commissioner for Patents, Washington, D.C. 20231, on

June 2nd, 2000.
(Date)

Polly C. Owen
Polly C. Owen

JC542 U.S. PTO
09/586370
06/02/00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: John D. Hottovy et al.

For: HIGH SOLIDS SLURRY POLYMERIZATION APPARATUS

"Express Mail" Mailing Label Number: EJ322669767US

Date of Deposit: June 2nd, 2000

CERTIFICATE OF MAILING BY "EXPRESS MAIL"

Assistant Commissioner for Patents
Washington, D. C. 20231

Sir:

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office To Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: John D. Hottovy et al.

Prior Application:	08/893,200
Examiner:	C. Lu Rutt
Group Art Unit:	1713

For: HIGH SOLIDS SLURRY POLYMERIZATION

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Please amend the application as follows:

In the Title

Please delete the title, and insert --- HIGH SOLIDS SLURRY POLYMERIZATION APPARATUS ---.

In the Specification

On page 1, upper right hand corner of page, and the upper right hand corner of each page thereafter, please change the attorney docket number "33591US" to --- 33591US1 ---.

On Page 1, line 1, please insert --- This application is a Divisional of application Serial No. 08/893,200, now pending. ---.

Please delete the Abstract and insert

--- A loop reactor apparatus comprising a plurality of vertical segments, a plurality of upper horizontal segments, and a plurality of lower horizontal segments. Each of the vertical segments is connected at an upper end thereof by a smooth upper bend to one of the upper horizontal segments, and is connected at a lower end thereof by a smooth lower bend to one of the lower horizontal segments thus defining a continuous flow path adapted to convey a fluid slurry, the reactor being substantially free from internal obstructions. The apparatus includes a means for introducing monomer reactant, polymerization catalyst and diluent into said reactor, a means for continuously moving said slurry along the flow path, and at least one elongated hollow appendage adjacent a downstream end of one of the lower horizontal sections. The appendage is in open communication with the flow path for continuously withdrawing product slurry. ---

In the Specification

On page 8, line 8, please delete "my", and insert --- by ---.

On page 12, line 15, please insert the following paragraph.

--- In another embodiment of this invention, a polymerization process is provided. The process comprises: 1) polymerizing, in a loop reaction zone, at least one olefin monomer in a liquid diluent to produce a fluid slurry, wherein the fluid slurry comprises liquid diluent and solid olefin polymer particles; 2) withdrawing the fluid slurry comprising withdrawn liquid diluent and withdrawn

solid polymer particles by alternately carrying out the following steps: a) allowing the fluid slurry to settle into at least one settling zone and thereafter withdrawing a batch of the thus settled slurry from the settling zone as an intermediate product of the process, thereafter shutting off the settling zone; and b) thereafter continuously withdrawing the fluid slurry comprising withdrawn liquid diluent and withdrawn solid polymer particles as an intermediate product of the process. In step b), the reactor conditions can be adjusted during startup to raise reactor solids by at least 10%. ---

On page 15, line 3 after the first "foot", please insert --- slurry height ---.

On page 15, line 7, please delete "The units for the pressure are ft/ft which cancel out".

On page 15, line 8, after "0.6", insert --g/cc--.

On page 15, line 10, please delete the first "which is the".

In the Claims

Please delete claims 1-23.

Remarks

Applicants respectfully request that the Examiner enter this Preliminary Amendment into the record.

Respectfully submitted

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HIGH SOLIDS SLURRY POLYMERIZATION

BACKGROUND OF THE INVENTION

This invention relates to the polymerization of olefin monomers in a liquid diluent.

Addition polymerizations are frequently carried out in a liquid which is a solvent for the resulting polymer. When high density (linear) ethylene polymers first became commercially available in the 1950's this was the method used. It was soon discovered that a more efficient way to produce such polymers was to carry out the polymerization under slurry conditions. More specifically, the polymerization technique of choice became continuous slurry polymerization in a pipe loop reactor with the product being taken off by means of settling legs which operated on a batch principle to recover product. This technique has enjoyed international success with billions of pounds of ethylene polymers being so produced annually. With this success has come the

desirability of building a smaller number of large reactors as opposed to a larger number of small reactors for a given plant capacity.

Settling legs, however, do present two problems. First, they represent the imposition of a "batch" technique onto a basic continuous process. Each time a settling leg reaches the stage where it "dumps" or "fires" accumulated polymer slurry it causes an interference with the flow of slurry in the loop reactor upstream and the recovery system downstream. Also the valve mechanism essential to periodically seal off the settling legs from the reactor upstream and the recovery system downstream requires frequent maintenance due to the difficulty in maintaining a tight seal with the large diameter valves needed for sealing the legs.

Secondly, as reactors have gotten larger, logistic problems are presented by the settling legs. If a pipe diameter is doubled the volume of the reactor goes up four-fold. However, because of the valve mechanisms involved, the size of the settling legs cannot easily be increased further. Hence the number of legs required begins to exceed the physical space available.

In spite of these limitations, settling legs have continued to be employed where olefin polymers are formed as a slurry in a liquid diluent. This is because, unlike bulk slurry polymerizations (i.e. where the monomer is the diluent) where solids concentrations of better than 60 percent are routinely obtained, olefin polymer slurries in a diluent are generally limited to no more

than 37 to 40 weight percent solids. Hence settling legs have been believed to be necessary to give a final slurry product at the exit to the settling legs of greater than 37-40 percent. This is because, as the name implies, settling occurs in the legs to thus increase the solids concentration of the slurry finally recovered as product slurry.

Another factor affecting maximum practical reactor solids is circulation velocity, with a higher velocity for a given reactor diameter allowing for higher solids since a limiting factor in the operation is reactor fouling due to polymer build up in the reactor.

SUMMARY OF THE INVENTION

It is an object of this invention to produce olefin polymers as a slurry in a liquid diluent utilizing continuous product slurry takeoff;

It is a further object of this invention to operate a slurry olefin polymerization process in a diluent at a reactor solids concentration high enough to make direct continuous product takeoff commercially viable;

It is a further object of this invention to operate a slurry olefin polymerization process in a diluent at higher circulation velocities.

It is yet a further object of this invention to operate a slurry olefin polymerization process in a diluent in a reaction zone of greater than 30,000 gallons; and

It is still yet a further object of this invention to provide a loop reactor apparatus having a capacity of greater than 30,000 gallons and having a continuous take off means.

In accordance with one aspect of this invention, an olefin polymerization process is carried out at a higher reactor solids concentration by means of continuous withdrawal of product slurry.

In accordance with another aspect of this invention, a loop reactor olefin polymerization process is carried out by operating at a higher circulation velocity for a given reactor pipe diameter.

In accordance with another aspect of this invention, a loop polymerization apparatus is provided having an elongated hollow appendage at a downstream end of one of the longitudinal segments of the loop, the hollow appendage being in direct fluid communication with a heated flash line and thus being adapted for continuous removal of product slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, forming a part hereof, Fig. 1 is a schematic perspective view of a loop reactor and polymer recovery system; Fig. 2 is cross section along line 2-2 of Fig. 1 showing a continuous take off appendage; Fig. 3 is a cross section along line 3-3 of Fig 2 showing a ram valve arrangement in the continuous take off assembly; Fig. 4 is a cross section of a tangential location for the continuous take off assembly; Fig. 5 is a side view of an elbow

of the loop reactor showing both a settling let and continuous take off assemblies; Fig. 6 is a cross section across line 6-6 of Fig. 5 showing the orientation of two of the continuous take off assemblies; Fig. 7 is a side view showing another orientation for the continuous take off assembly; Fig. 8 is a cross sectional view of the impeller mechanism; Fig. 9 is a schematic view showing another configuration for the loops wherein the upper segments 14a are 180 degree half circles and wherein the vertical segments are at least twice as long as the horizontal segments and Fig. 10 is a schematic view showing the longer axis disposed horizontally.

DETAILED DESCRIPTION OF THE INVENTION

Surprisingly, it has been found that continuous take off of product slurry in an olefin polymerization reaction carried out in a loop reactor in the presence of an inert diluent allows operation of the reactor at a much higher solids concentration. Commercial production of predominantly ethylene polymers in isobutane diluent has generally been limited to a maximum solids concentration in the reactor of 37-40 weight percent. However, the continuous take off has been found to allow significant increases in solids concentration. Furthermore, the continuous take off itself brings about some additional increase in solids content as compared with the content in the reactor from which it takes off product because of the placement of the continuous take off appendage which selectively removes a slurry from a stratum where the solids

are more concentrated. Hence concentrations of greater than 40 weight percent are possible in accordance with this invention.

Throughout this application, the weight of catalyst is disregarded since the productivity, particularly with chromium oxide on silica, is extremely high.

Also surprisingly, it has been found that more aggressive circulation (with its attendant higher solids concentration) can be employed. Indeed more aggressive circulation in combination with the continuous take off, solids concentrations of greater than 50 weight percent can be removed from the reactor by the continuous take off. For instance, the continuous take off can easily allow operating at 5-6 percentage points higher; i.e., the reactor can be adjusted to easily raise solids by 10 percent; and the more aggressive circulation can easily add another 7-9 percentage points which puts the reactor above 50 percent. But, because the continuous take off is positioned to take off slurry from a stratum in the stream which has a higher than average concentration of solids, the product actually recovered has about 3 percentage points(or greater) higher concentration than the reactor slurry average. Thus the operation can approach an effective slurry concentration of 55 weight percent or more, i.e. 52 percent average in the reactor and the removal of a component which is actually 55 percent (i.e. 3 percentage points) higher.

It must be emphasized that in a commercial operation as little as a one percentage point increase in solids concentration is of major significance. Therefore going from 37-40 average percent solids concentration in the reactor to even 41 is important; thus going to greater than 50 is truly remarkable.

The present invention is applicable to any olefin polymerization in a loop reactor utilizing a diluent so as to produce a product slurry of polymer and diluent. Suitable olefin monomers are 1-olefins having up to 8 carbon atoms per molecule and no branching nearer the double bond than the 4-position. The invention is particularly suitable for the homopolymerization of ethylene and the copolymerization of ethylene and a higher 1-olefin such as butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Especially preferred is ethylene and 0.01 to 10, preferably 0.01 to 5, most preferably 0.1 to 4 weight percent higher olefin based on the total weight of ethylene and comonomer. Alternatively sufficient comonomer can be used to give the above-described amounts of comonomer incorporation in the polymer.

Suitable diluents (as opposed to solvents or monomers) are well known in the art and include hydrocarbons which are inert and liquid under reaction conditions. Suitable hydrocarbons include isobutane, propane, n-pentane, i-pentane, neopentane and n-hexane, with isobutane being especially preferred.

Suitable catalysts are well known in the art. Particularly suitable is chromium oxide on a support such as silica as broadly disclosed, for instance, in Hogan and Banks, US 2,285,721 (March 1958) , the disclosure of which is hereby incorporated by reference.

Referring now to the drawings, there is shown in Fig. 1 a loop reactor **10** having vertical segments **12**, upper horizontal segments **14** and lower horizontal segments **16**. These upper and lower horizontal segments define upper and lower zones of horizontal flow. The reactor is cooled my means of two pipe heat exchangers formed by pipe **12** and jacket **18**. Each segment is connected to the next segment by a smooth bend or elbow **20** thus providing a continuous flow path substantially free from internal obstructions. The polymerization mixture is circulated by means of impeller **22** (shown in Fig. 8) driven by motor **24**. Monomer, comonomer, if any, and make up diluent are introduced via lines **26** and **28** respectively which can enter the reactor directly at one or a plurality of locations or can combine with condensed diluent recycle line **30** as shown. Catalyst is introduced via catalyst introduction means **32** which provides a zone (location) for catalyst introduction. The elongated hollow appendage for continuously taking off an intermediate product slurry is designated broadly by reference character **34**. Continuous take off mechanism **34** is located in or adjacent to a downstream end of one of the lower horizontal reactor loop sections **16** and adjacent or on a connecting elbow **20**.

The continuous take off appendage is shown at the downstream end of a lower horizontal segment of the loop reactor which is the preferred location. The location can be in an area near the last point in the loop where flow turns upward before the catalyst introduction point so as to allow fresh catalyst the maximum possible time in the reactor before it first passes a take off point. However, the continuous take off appendage can be located on any segment or any elbow.

Also, the segment of the reactor to which the continuous take off appendage is attached can be of larger diameter to slow down the flow and hence further allow stratification of the flow so that the product coming off can have an even greater concentration of solids.

The continuously withdrawn intermediate product slurry is passed via conduit **36** into a high pressure flash chamber **38**. Conduit **36** includes a surrounding conduit **40** which is provided with a heated fluid which provides indirect heating to the slurry material in flash line conduit **36**. Vaporized diluent exits the flash chamber **38** via conduit **42** for further processing which includes condensation by simple heat exchange using recycle condenser **50**, and return to the system, without the necessity for compression, via recycle diluent line **30**. Recycle condenser **50** can utilized any suitable heat exchange fluid known in the art under any conditions known in the art. However preferably a fluid at a temperature that can be economically provided is used. A suitable

temperature range for this fluid is 40 degrees F to 130 degrees F. Polymer particles are withdrawn from high pressure flash chamber **38** via line **44** for further processing using techniques known in the art. Preferably they are passed to low pressure flash chamber **46** and thereafter recovered as polymer product via line **48**. Separated diluent passes through compressor **47** to line **42**. This high pressure flash design is broadly disclosed in Hanson and Sherk, US 4,424,341 (Jan. 3, 1984), the disclosure of which is hereby incorporated by reference. Surprisingly, it has been found that the continuous take off not only allows for higher solids concentration upstream in the reactor, but also allows better operation of the high pressure flash, thus allowing the majority of the withdrawn diluent to be flashed off and recycled with no compression. Indeed, 70 to 90 percent of the diluent can generally be recovered in this manner. This is because of several factors. First of all, because the flow is continuous instead of intermittent, the flash line heaters work better. Also, the pressure drop after the proportional control valve that regulates the rate of continuous flow out of the reactor has a lower pressure which means when it flashes it drops the temperature lower thus further giving more efficient use of the flash line heaters.

Referring now to Fig. 2, there is shown elbow **20** with continuous take off mechanism **34** in greater detail. The continuous take off mechanism comprises a take off cylinder **52**, a slurry withdrawal line **54**, an emergency

shut off valve **55**, a proportional motor valve **58** to regulate flow and a flush line **60**. The reactor is run "liquid" full. Because of dissolved monomer the liquid has slight compressibility, thus allowing pressure control of the liquid full system with a valve. Diluent input is generally held constant, the proportional motor valve **58** being used to control the rate of continuous withdrawal to maintain the total reactor pressure within designated set points.

Referring now to Fig. 3, which is taken along section line 3-3 of Fig. 2, there is shown the smooth curve or elbow **20** having associated therewith the continuous take off mechanism **34** in greater detail, the elbow **20** thus being an appendage-carrying elbow. As shown, the mechanism comprises a take off cylinder **52** attached, in this instance, at a right angle to a tangent to the outer surface of the elbow. Coming off cylinder **52** is slurry withdrawal line **54**. Disposed within the take off cylinder **52** is a ram valve **62** which serves two purposes. First it provides a simple and reliable clean-out mechanism for the take off cylinder if it should ever become fouled with polymer. Second, it can serve as a simple and reliable shut-off valve for the entire continuous take off assembly.

Figure 4 shows a preferred attachment orientation for the take off cylinder **52** wherein it is affixed tangentially to the curvature of elbow **20** and at a point just prior to the slurry flow turning upward. This opening is elliptical to

the inside surface. Further enlargement could be done to improve solids take off.

Figure 5 shows four things. First, it shows an angled orientation of the take off cylinder **52**. The take off cylinder is shown at an angle, alpha, to a plane that is (1) perpendicular to the centerline of the horizontal segment **16** and (2) located at the downstream end of the horizontal segment **16**. The angle with this plane is taken in the downstream direction from the plane. The apex for the angle is the center point of the elbow radius as shown in Fig. 5. The plane can be described as the horizontal segment cross sectional plane. Here the angle depicted is about 24 degrees. Second, it shows a plurality of continuous take off appendages, **34** and **34a**. Third, it shows one appendage, **34** oriented on a vertical center line plane of lower segment **16**, and the other, **34a**, located at an angle to such a plane as will be shown in more detail in Fig. 6. Finally, it shows the combination of continuous take off appendages **34** and a conventional settling leg **64** for batch removal, if desired.

As can be seen from the relative sizes, the continuous take off cylinders are much smaller than the conventional settling legs. Yet three 2-inch ID continuous take off appendages can remove as much product slurry as 14 8-inch ID settling legs. This is significant because with current large commercial loop reactors of 15,000-18000 gallon capacity, six eight inch settling legs are required. It is not desirable to increase the size of the settling legs because of

the difficulty of making reliable valves for larger diameters. As noted previously, doubling the diameter of the pipe increases the volume four-fold and there simply in not enough room for four times as many settling legs to be easily positioned. Hence the invention makes feasible the operation of larger, more efficient reactors. Reactors of 30,000 gallons or greater are made possible by this invention. Generally the continuous take off cylinders will have a nominal internal diameter within the range of 1 inch to less than 8 inches. Preferably they will be about 2-3 inches internal diameter.

Figure 6 is taken along section line 6-6 of Fig. 5 and shows take off cylinder **34a** attached at a place that is oriented at an angle, beta, to a vertical plane containing the center line of the reactor. This plane can be referred to as the vertical center plane of the reactor. This angle can be taken from either side of the plane or from both sides if it is not zero. The apex of the angle is located at the reactor center line. The angle is contained in a plane perpendicular to the reactor center line as shown in Fig. 6.

It is noted that there are three orientation concepts here. First is the attachment orientation, i.e. tangential as in Fig. 4 and perpendicular as in Fig. 2 or 7 or any angle between these two limits of 0 and 90 degrees. Second is the orientation relative to how far up the curve of the elbow the attachment is as represented by angle alpha (Fig. 5). This can be anything from 0 to 60 degrees but is preferably 0 to 40 degrees, more preferably 0 to 20 degrees.

Third is the angle, beta, from the center plane of the longitudinal segment (Fig. 6). This angle can be from 0 to 60 degrees, preferably 0 to 45 degrees, more preferably 0-20 degrees.

Fig. 7 shows an embodiment where the continuous take off cylinder **52** has an attachment orientation of perpendicular, an alpha orientation of 0 (inherent since it is at the end, but still on, the straight section), and a beta orientation of 0, i.e. it is right on the vertical centerline plane of the lower horizontal segment **16**.

Fig. 8 shows in detail the impeller means **22** for continuously moving the slurry along its flow path. As can be seen in this embodiment the impeller is in a slightly enlarged section of pipe which serves as the propulsion zone for the circulating reactants. Preferably the system is operated so as to generate a pressure differential of at least 18 psig preferably at least 20 psig, more preferably at least 22 psig between the upstream and downstream ends of the propulsion zone in a nominal two foot diameter reactor with total flow path length of about 950 feet using isobutane to make predominantly ethylene polymers. As much as 50 psig or more is possible. This can be done by controlling the speed of rotation of the impeller, reducing the clearance between the impeller and the inside wall of the pump housing or by using a more aggressive impeller design as is known in the art. This higher pressure differential can also be produced by the use of at least one additional pump.

Generally the system is operated so as to generate a pressure differential, expressed as a loss of pressure per unit length of reactor, of at least 0.07, generally 0.07 to 0.15 foot pressure drop per foot of reactor length for a nominal 24 inch diameter reactor. Preferably, this pressure drop per unit length is 0.09 to 0.11 for a 24 inch diameter reactor. For larger diameters, a higher slurry velocity and a higher pressure drop per unit length of reactor is needed. The units for the pressure are ft/ft which cancel out. This assumes the density of the slurry which generally is about 0.5 - 0.6.

Referring now to Fig. 9 the upper segments are shown as 180 degree half circles which is the which is the preferred configuration. The vertical segments are at least twice the length, generally about seven to eight times the length of the horizontal segments. For instance, the vertical flow path can be 190 - 225 feet and the horizontal segments 25 - 30 feet in flow path length. Any number of loops can be employed in addition to the four depicted here and the eight depicted in Fig. 1, but generally four or six are used. Reference to nominal two foot diameter means an internal diameter of about 21.9 inches. Flow length is generally greater than 500 feet, generally greater than 900 feet, with about 940 to 1,350 feet being quite satisfactory.

Commercial pumps for utilities such as circulating the reactants in a closed loop reactor are routinely tested by their manufacturers and the necessary pressures to avoid cavitation are easily and routinely determined.

EXAMPLES

A four vertical leg polymerization reactor using a 26 inch Lawrence Pumps Inc. pump impeller D51795/81-281 in a M51879/FAB casing was used to polymerize ethylene and hexene-1. This pump was compared with a 24 inch pump which gave less aggressive circulation (0.66 ft of pressure drop vs 0.98). This was then compared with the same more aggressive circulation and a continuous take off assembly of the type shown by reference character 34 of Fig. 5. The results are shown below.

DATA TABLE			
Description	**24 in Pump**	**26 in Pump**	**26 in Pump + CTO**
Date of Operation	Oct 4-9, 1994	May 24-28, 1995	Nov 15-18, 1996
Avg. Reactor Solids Concentration, wt %	39	45	53
Polymer Production Rate, mlbs/hr	40.1	40.7	39.9
Reactor Circulation Pump Power, kw	430	691	753
Circulation Pump Pressure Diff, psi	14.3	22.4	23.7
Circulation Pump Head, ft	61.8	92.5	92.4
Reactor Slurry Flow Rate, mGPM	39	46	45
Reactor Slurry Density, gm/cc	0.534	0.558	0.592
Reactor Temperature, F	215.6	218.3	217.0
Ethylene Concentration, wt %	4.43	3.67	4.9
Hexene-1 Concentration, wt %	0.22	0.17	0.14
Reactor Heat Transfer Coefficient	270	262	241
Reactor Inside Diameter, inches	22.0625	22.0625	22.0625
Reactor Volume, gal	18700	18700	18700
Reactor Length, ft	941	941	941
Pressure Drop per Foot of Reactor, ft/ft	0.066	0.098	0.098

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby, but is intended to cover all changes within the spirit and scope thereof.

THAT WHICH IS CLAIMED IS:

1. A polymerization process comprising:

polymerizing, in a loop reaction zone, at least one olefin monomer in a liquid diluent to produce a fluid slurry comprising liquid diluent and solid olefin polymer particles;

maintaining a concentration of said solid olefin polymer particles in said slurry in said zone of greater than 40 weight percent based on the weight of said polymer particles and the weight of said liquid diluent;

continuously withdrawing said slurry comprising withdrawn liquid diluent and withdrawn solid polymer particles as an intermediate product of said process.

2. A process according to claim 1 wherein said olefin monomer comprises ethylene.

3. A process according to claim 1 wherein said olefin monomer comprises ethylene and 0.01-5 weight percent hexene based on the total weight of said ethylene and said hexene, and wherein said liquid diluent is cyclohexane.

4. A process according to claim 3 wherein said concentration of said solid olefin polymer particles in said slurry in said zone is greater than 50 weight percent based on the weight of said polymer particles and the weight of said liquid diluent.

5. A process according to claim 1 wherein a pressure differential of at least 18 psig is maintained in a propulsion zone to circulate said slurry through said reaction zone.

6. A process according to claim 1 wherein a pressure differential of greater than 0.07 per foot of reactor flow path length is maintained in a propulsion zone.

7. A process according to claim 6 wherein said differential is within the range of 0.07 to 0.15 ft/ft per foot of said reactor flow path length.

8. A process according to claim 1 wherein said reaction zone is maintained liquid full.

9. A process according to claim 1 wherein said reaction zone has a volume of greater than 20,000 gallons.

10. A process according to claim 1 wherein said reaction zone has a volume of greater than 30,000 gallons.

11. A process according to claim 1 wherein said intermediate product of said process is continuously passed through a heating zone wherein said intermediate product is heated to produce a heated intermediate product and thereafter said heated intermediate product is exposed to a pressure drop in a high pressure flash zone, said heated intermediate product being heated to an extent such that a major portion of said withdrawn liquid diluent is vaporized and thus separated from said withdrawn solid polymer particles, the thus

separated withdrawn liquid diluent thereafter being condensed for recycle, without any compression, by heat exchange with a fluid having a temperature within the range of about 40 degrees F to about 130 degrees F.

12. A process according to claim 1 wherein said slurry is continuously withdrawn from an area near the last point in said loop reaction zone where flow turns upward before a catalyst introduction zone.

13. A process according to claim 1 wherein said slurry is continuously withdrawn from at least one area adjacent the end of a lower zone of horizontal flow.

14. A process according to claim 13 wherein said slurry is withdrawn at a point along the vertical centerline plane of said lower zone of horizontal flow and prior to said flow turning upward.

15. A process according to claim 13 wherein said at least one area is along the vertical centerline plane of said lower zone of horizontal flow and after said flow has turned upward.

16. A process according to claim 13 wherein said at one area is oriented at an angle away from the vertical center plane of said lower zone of horizontal flow an amount within the range of 0 degrees to 45 degrees.

17. A process according to claim 16 wherein said at least one area is oriented away from said vertical center plane at an angle within the range of 0 degrees to 20 degrees.

18. A process according to claim 16 wherein said at least one area is prior to said flow turning upward.

19. A process according to claim 16 wherein said at least one area is at a location after said flow has turned upward at least 1 but less than 45 degrees from a centerline of upward flow.

20. A process according to claim 13 wherein said at least one area is exactly one area.

21. A process according to claim 13 wherein said at least one area is a plurality of areas.

22. A polymerization process comprising:

polymerizing, in a loop reaction zone, at least one olefin monomer in a liquid diluent to produce a fluid slurry comprising liquid diluent and solid olefin polymer particles;

withdrawing said slurry comprising withdrawn liquid diluent and withdrawn solid polymer particles by alternately carrying out the following steps:

(A) allowing said slurry to settle into at least one settling zone and thereafter withdrawing a batch of the thus settled slurry from said settling zone as an intermediate product of said process, thereafter shutting off said settling zone; and

(B) thereafter continuously withdrawing said slurry comprising withdrawn liquid diluent and withdrawn solid polymer particles as an intermediate product of said process.

23. A process according to claim 22 comprising in addition adjusting reactor conditions during startup of step (B) to raise reactor solids by at least 10 percent.

24. A loop reactor apparatus comprising:

a plurality of vertical segments;

a plurality of upper horizontal segments;

a plurality of lower horizontal segments;

wherein each of said vertical segments is connected at an upper end thereof by a smooth upper bend to one of said upper horizontal segments, and is connected at a lower end thereof by a smooth lower bend to one of said lower horizontal segments thus defining a continuous flow path adapted to convey a fluid slurry, said reactor being substantially free from internal obstructions;

means for introducing monomer reactant, polymerization catalyst and diluent into said reactor;

means for continuously moving said slurry along said flow path;

at least one elongated hollow appendage adjacent a downstream end of one of said lower horizontal sections, said appendage being in open

communication with said flow path for continuously withdrawing product slurry; and

an elongated flash line in fluid communication with said appendage for transferring product slurry from said appendage to a flash means, said flash line having a heater associated therewith to heat said product slurry.

25. An apparatus according to claim 24 wherein said at least one appendage is attached to one of said lower horizontal segments thus giving an appendage-carrying lower horizontal segment, said appendage being oriented along a vertical centerline plane of said appendage-carrying lower horizontal segment and adjacent to the smooth lower bend attached to the downstream end of said appendage-carrying lower horizontal segment.

26. Apparatus according to claim 24 wherein said appendage is attached at an angle between 0 and 90 degrees.

27. An apparatus according to claim 24 wherein said at least one appendage is attached to said smooth bend attached to said downstream end of said appendage-carrying lower horizontal segment thus giving an appendage-carrying smooth bend.

28. An apparatus in accordance in accordance with claim 27 wherein said appendage is attached to said appendage-carrying smooth bend at

a point at least 1 but less than 45 degrees from a centerline of the adjacent vertical segment.

29. Apparatus according to claim 31 wherein said appendage is attached at an angle between 0 and 90 degrees.

30. Apparatus according to claim 28 wherein said at least one appendage is attached at a right angle to a tangent to said appendage-carrying bend.

31. Apparatus according to claim 28 wherein said at least one appendage is attached tangentially to said appendage-carrying bend.

32. Apparatus according to claim 31 wherein said at least one appendage is attached at a point spaced away from said vertical center plane an amount within the range of 20-45 degrees.

33. Apparatus according to claim 31 wherein said at least one appendage is exactly one appendage.

34. Apparatus according to claim 31 wherein said at least one appendage is a plurality of appendages.

ABSTRACT OF THE DISCLOSURE

An olefin polymerization process wherein monomer, diluent and catalyst are circulated in a continuous loop reactor and product slurry is recovered by means of a continuous product take off. The continuous product allows operating the reaction at significantly higher solids content in the circulating slurry. In a preferred embodiment, the slurry is heated in a flash line heater and passed to a high pressure flash where a majority of the diluent is separated and thereafter condensed by simple heat exchange, without compression, and thereafter recycled. Also an olefin polymerization process operating at higher reactor solids by virtue of more aggressive circulation.

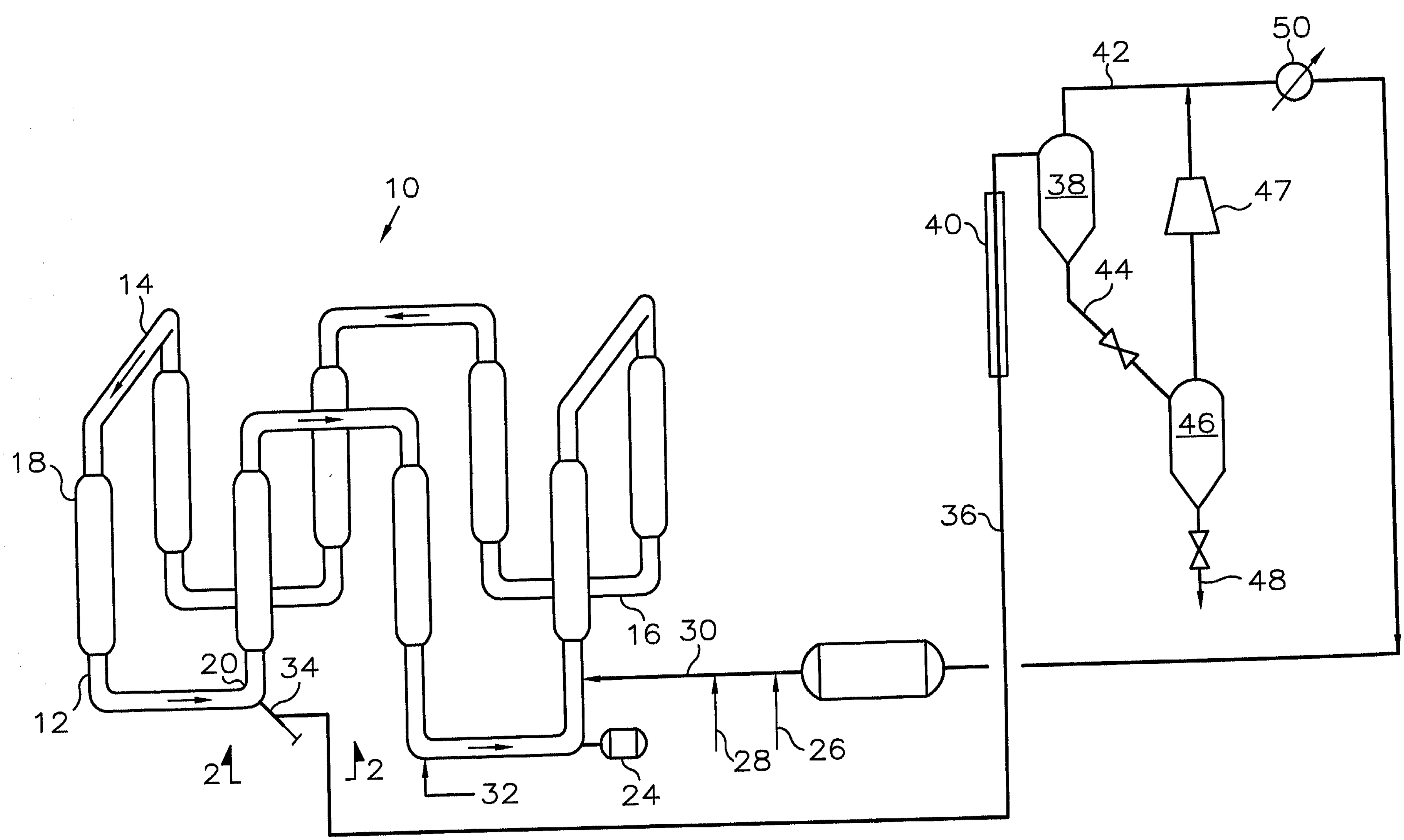

FIG. 1

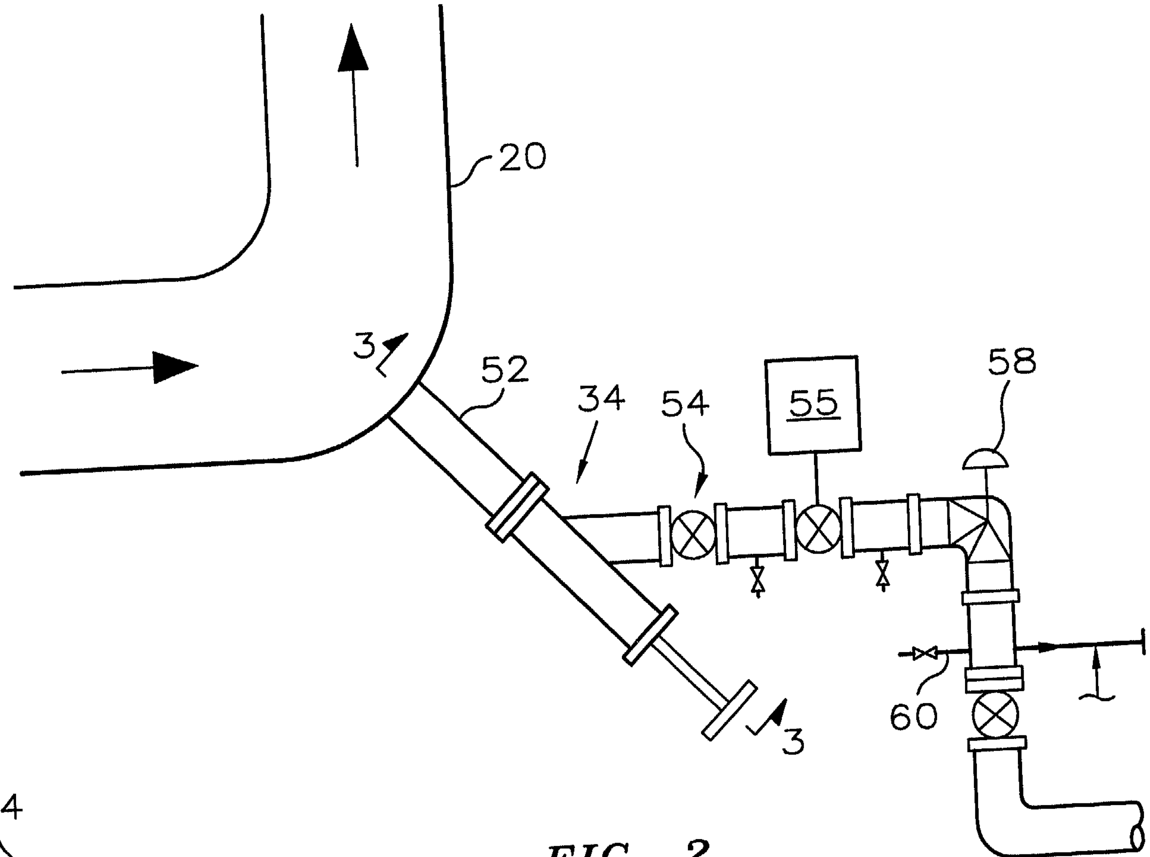

FIG. 2

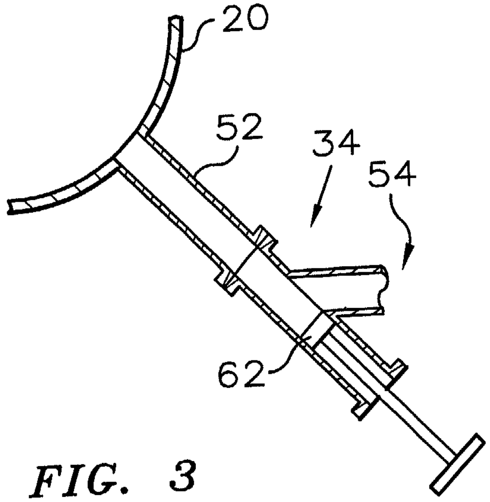

FIG. 3

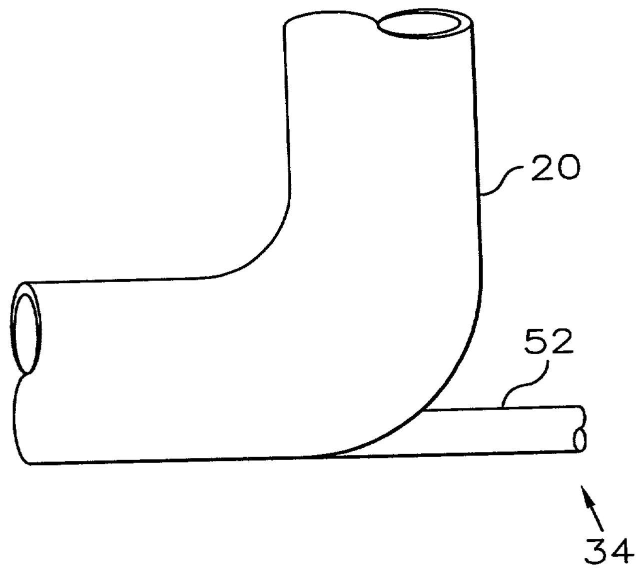

FIG. 4

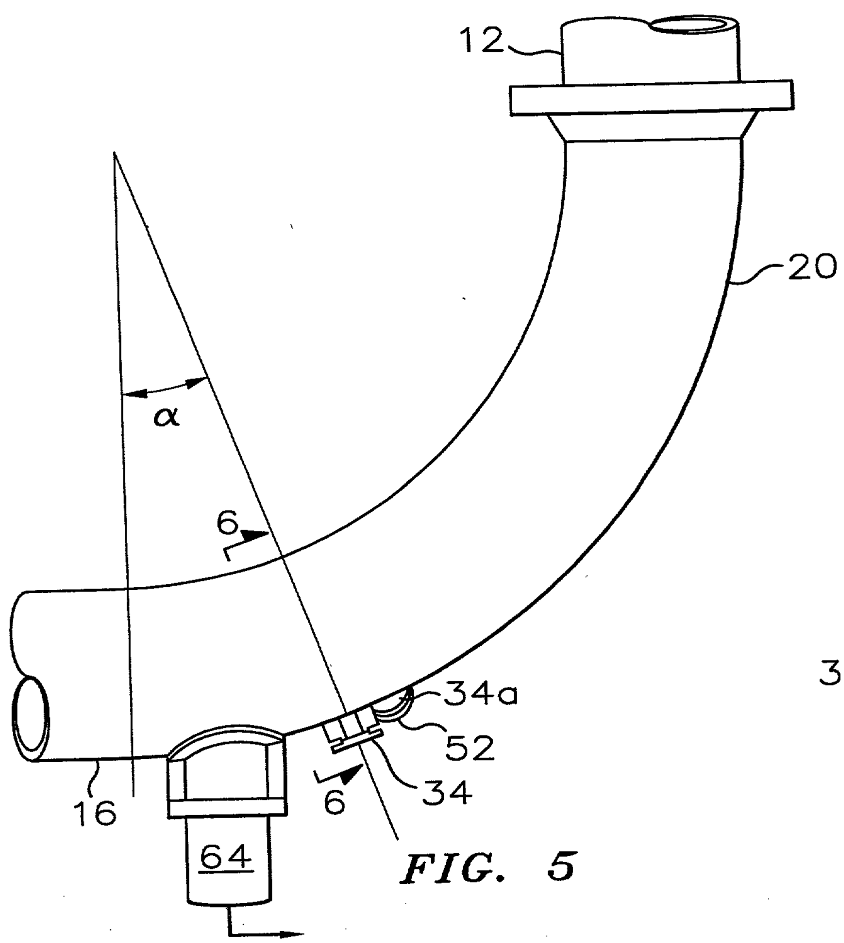

FIG. 5

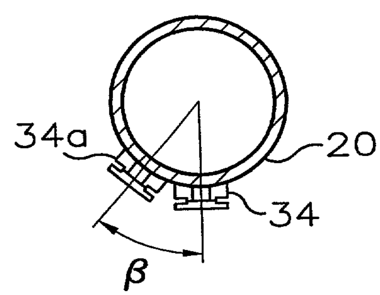

FIG. 6

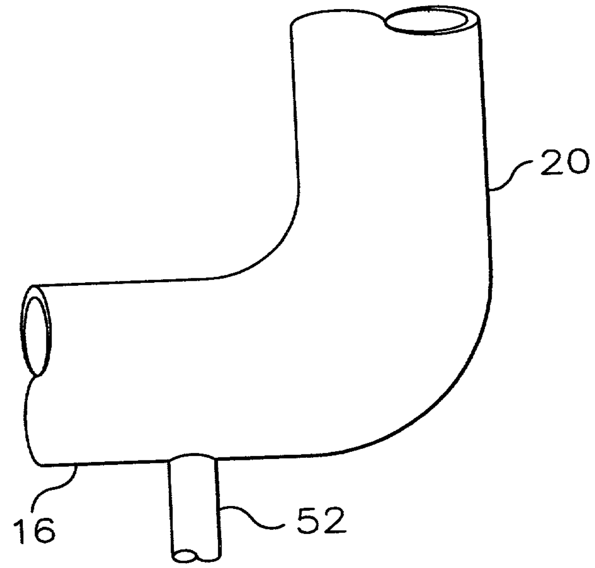

FIG. 7

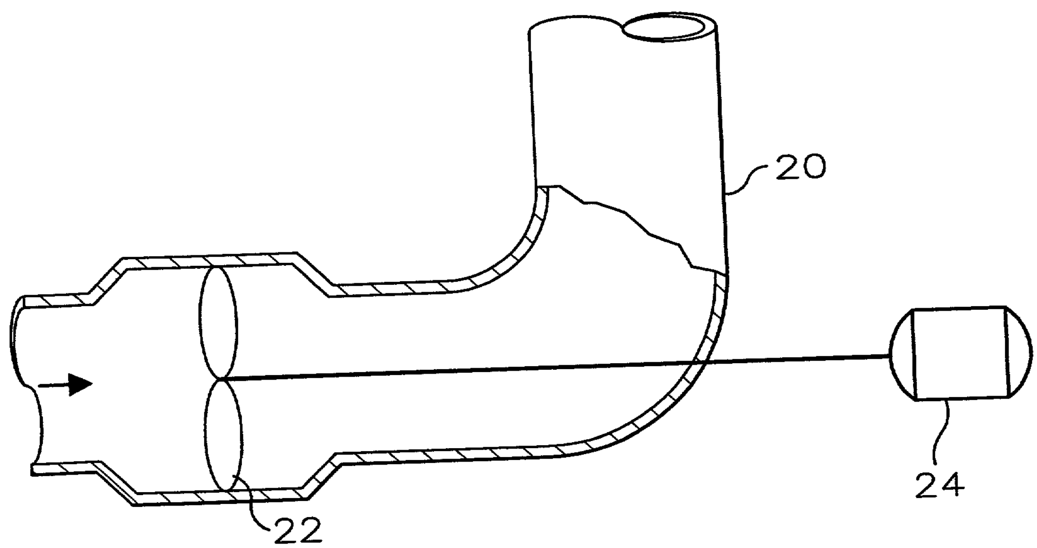

FIG. 8

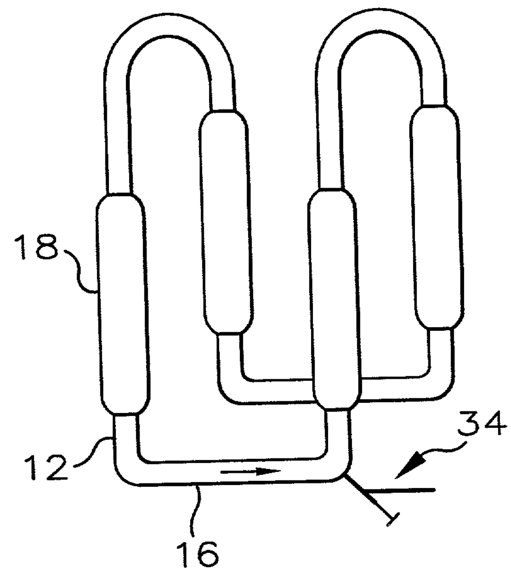

FIG. 9

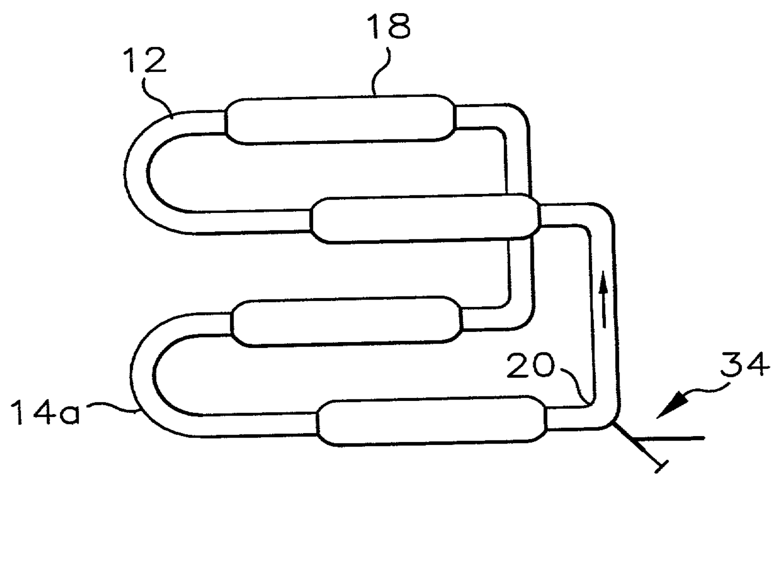

FIG. 10

33591US

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, John D. Hottovy, declare:

that I am a citizen of the United States of America residing at 2816 Claremont, Bartlesville, Oklahoma 74006 and having a post office address of 2816 Claremont, Bartlesville, Oklahoma 74006;

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, Harvey D. Hensley, David J. Przelomski, Teddy H. Cymbaluk, Robert K. Franklin, III and Ethelwoldo P. Perez are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

and I hereby appoint Edward L. Bowman, Registration No. 27,116; Carl D. Corvin, Registration No. 34,569; Ryan N. Cross, Registration No. 33,861; Beverly M. Dollar, Registration No. 32,870; John M. Fish, Jr., Registration No. 25,863; Gary L. Haag, Registration No. 35,529; Bion E. Hitchcock, Registration No. 26,613; Lynda S. Jolly, Registration No. 32,736; Allen W. Richmond, Registration No. 28,662; Lucas K. Shay, Registration No. 34,724; and Charles W. Stewart, Registration No. 34,023; who comprise the firm of **Richmond, Hitchcock, Fish & Dollar, P. O. Box 2443, Bartlesville, Oklahoma, 74005,** Registration No. 20,286; and Archie W. Umphlett, Registration No. 25,935, each attorney a member of the Bar of the State of Oklahoma or the District of Columbia; my representatives with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Wherefore I pray that Letters Patent be granted to Phillips Petroleum Company, a corporation organized and existing under the laws of the State of Delaware and domiciled and having an office at Bartlesville, Oklahoma, as assignee, for the invention or discovery described and claimed in the foregoing specification and claims, and I hereby subscribe my name to the foregoing specification and claims, declaration, power of attorney and this petition.

Correspondence Address:
c/o **RICHMOND, HITCHCOCK,**
FISH & DOLLAR
P.O. Box 2443
Bartlesville, Oklahoma 74005

Inventor ____________
John D. Hottovy

Date 7/12/97

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, Harvey D. Hensley, declare:

that I am a citizen of the United States of America residing at 2527 Dorchester, Bartlesville, Oklahoma 74006 and having a post office address of 2527 Dorchester, Bartlesville, Oklahoma 74006;

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, John D. Hottovy, David J. Przelomski, Teddy H. Cymbaluk, Robert K. Franklin, III and Ethelwoldo P. Perez are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

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Inventor Harvey D. Hensley
Harvey D. Hensley

Date 7/13/97

Correspondence Address:
c/o RICHMOND, HITCHCOCK, FISH & DOLLAR
P.O. Box 2443
Bartlesville, Oklahoma 74005

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, David J. Przelomski, declare:

that I am a citizen of the United States of America residing at 14419 Fair Knoll Way, Houston, Texas 77062 and having a post office address of 14419 Fair Knoll Way, Houston, Texas 77062;

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, John D. Hottovy, Harvey D. Hensley, Teddy H. Cymbaluk, Robert K. Franklin, III and Ethelwoldo P. Perez are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

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Correspondence Address:
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FISH & DOLLAR
P.O. Box 2443
Bartlesville, Oklahoma 74005

Inventor David J. Przelomski
David J. Przelomski

Date 7/14/97

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, Teddy H. Cymbaluk, declare:

that I am a citizen of the United States of America residing at 1400 Jefferson Road, Pasadena, Texas 77501 and having a post office address of P.O. Box 823, Seabrook, Texas 77586;

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, John D. Hottovy, Harvey D. Hensley, David J. Przelomski, Robert K. Franklin, III and Ethelwoldo P. Perez are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

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Correspondence Address:
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P.O. Box 2443
Bartlesville, Oklahoma 74005

Inventor Teddy H. Cymbaluk
Teddy H. Cymbaluk

Date 7/14/97

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, Robert K. Franklin, III declare:

that I am a citizen of the United States of America residing at 4307 Roaring Rapids, Houston, Texas 77059 and having a post office address of 4307 Roaring Rapids, Houston, Texas 77059;

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, John D. Hottovy, Harvey D. Hensley, David J. Przelomski, Teddy H. Cymbaluk, and Ethelwoldo P. Perez are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

and I hereby appoint Edward L. Bowman, Registration No. 27,116; Carl D. Corvin, Registration No. 34,569; Ryan N. Cross, Registration No. 33,861; Beverly M. Dollar, Registration No. 32,870; John M. Fish, Jr., Registration No. 25,863; Gary L. Haag, Registration No. 35,529; Bion E. Hitchcock, Registration No. 26,613; Lynda S. Jolly, Registration No. 32,736; Allen W. Richmond, Registration No. 28,662; Lucas K. Shay, Registration No. 34,724; and Charles W. Stewart, Registration No. 34,023; who comprise the firm of **Richmond, Hitchcock, Fish & Dollar, P. O. Box 2443, Bartlesville, Oklahoma, 74005,** Registration No. 20,286; and Archie W. Umphlett, Registration No. 25,935, each attorney a member of the Bar of the State of Oklahoma or the District of Columbia; my representatives with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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Correspondence Address:
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P.O. Box 2443
Bartlesville, Oklahoma 74005

Inventor Robert K Franklin III
Robert K. Franklin, III

Date July 14, 1997

33591US

DECLARATION, POWER OF ATTORNEY, AND PETITION

To The Commissioner of Patents and Trademarks:

I, Ethelwoldo P. Perez declare:

that I am a citizen of the United States of America residing at 3303 Williams Glen Drive, Sugar Land, Texas 77479 and having a post office address of 3303 Williams Glen Drive, Sugar Land, Texas 77479

that I have reviewed and understand the contents of the attached specification and claims and I verily believe I, John D. Hottovy, Harvey D. Hensley, David J. Przelomski, Teddy H. Cymbaluk, and Robert K. Franklin, III are the original, first, and joint inventors or discoverers of the invention or discovery in **HIGH SOLIDS SLURRY POLYMERIZATION** described and claimed therein and for which a patent is sought;

I acknowledge my duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations § 1.56;

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Inventor Ethelwoldo P. Perez
Ethelwoldo P. Perez

Date July 14, 1997

Correspondence Address:
c/o RICHMOND, HITCHCOCK,
FISH & DOLLAR
P.O. Box 2443
Bartlesville, Oklahoma 74005